

CERIUM PROMOTED NI/MGO CATALYST FOR GLYCEROL REFORMING

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ABSTARCT

Hydrogen (H_2) has been considered as energy of future to substitute fossil fuel utilization. It is currently produced from hydrocarbon reforming (i.e. natural gas and petroleum) and electrolysis processes. Therefore, in the current work, magnesium oxide (MgO)-supported Ni catalyst with Cerium, Ce as a promoter was prepared to produce the synthesis gas H_2 from the glycerol reforming reaction and the activity of catalyst is studied. Besides, the physicochemical properties of fresh catalysts were characterized with various techniques. BET characterization of both fresh 3 wt% and 5 wt% Ce-Ni/MgO catalysts showed that the 5 wt% Ce-Ni/MgO catalyst has larger BET specific surface area and pore diameter than the 3 wt% Ce-Ni/MgO catalyst. XRD diffraction pattern of fresh 5 wt% Ce-Ni/MgO catalyst showed peaks representing MgO at $2\theta = 37.00^\circ$ and NiO at 42.99° , 62.41° , 74.84° and 78.79° . From the FESEM imaging of 5 wt% Ce-Ni/MgO catalyst, it can be observed that it is a crystalline catalyst. TGA results summarized that the magnitude of the highest peak increases as the heating ramp increases from 10 to 20 $^\circ\text{C}/\text{min}$. Besides that, reaction studies have found that the 3 wt% catalysts gave almost equal rate of formation of product yield (H_2 and CO). From the results obtained, the glycerol conversion, X_G was directly proportional with the reactant (glycerol to N_2) flow ratios. Furthermore, the activation energy obtained for H_2 formation rate from the current study was 27.82 kJ/mol. The fairly low E_a indicated that the catalyst was very active in promoting the hydrogen production from the glycerol.

ABSTRAK

Hidrogen (H_2) telah dianggap sebagai tenaga alternative pada masa depan untuk menggantikan penggunaan bahan api fosil. Ia dihasilkan daripada hidrokarbon pembaharuan (iaitu gas asli dan petroleum) dan elektrolisis proses. Oleh itu, dalam kajian ini, magnesium oksida (MgO) disokong Ni pemangkin dengan Serium, Ce sebagai penganjur yang telah disediakan untuk menghasilkan gas H_2 sintesis dari gliserol pembaharuan dan aktiviti pemangkin juga ditelitikan. Selain itu, sifat-sifat fizikokimia pemangkin telah dicirikan dengan pelbagai teknik. BET pencirian bagi 3 wt% dan 5 wt% pemangkin segar Ce-Ni/MgO menunjukkan bahawa 5 wt% Ce-Ni/MgO pemangkin mengandungi kawasan permukaan spesifik dan diameter liang yang lebih besar daripada 3 wt% Ce-Ni/MgO. Selain itu, corak pembelauan XRD bagi 5 wt% Ce-Ni/MgO pemangkin pula menunjukkan puncak yang mewakili MgO di $2\theta = 37.00^\circ$ dan NiO pada 42.99° , 62.41° , 74.84° dan 78.79° . Dari keputusan pengimejan FESEM 5 wt% Ce-Ni/MgO, dapat diperhatikan bahawa ia merupakan pemangkin kristal. Keputusan TGA juga merumuskan bahawa magnitud puncak tertinggi meningkat apabila tanjakan pemanasan bertambah dari 10 hingga 20 $^\circ\text{C}/\text{min}$. Selain itu, kajian reaksi telah mendapati bahawa 3 wt% pemangkin memberikan kadar pembentukan hasil produk (H_2 dan CO) yang hampir sama. Sehubungan itu, keputusan tindak balas juga memaparkan bahawa purata penukaran gliserol, XG adalah sejajar dengan nisbah aliran bahan tindak balas (gliserol : N_2). Tambahan pula, tenaga pengaktifan, E_a yang diperolehi bagi kadar pembentukan H_2 daripada kajian ini adalah 27.82 kJ/mol. Tenaga pengaktifan yang agak rendah tersebut menunjukkan bahawa pemangkin sangat aktif dalam menggalakkan pembentukan gas H_2 daripada gliserol.

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LIST OF SYMBOLS

P	gas pressure
P_s	saturation pressure of the adsorbate gas
V	volume of gas adsorbed
V_m	volume of gas adsorbed corresponding to monolayer coverage
c	a characteristic constant of the adsorbate
S_A	surface area of solid
a_m	average area occupied by a molecule
n_m	monolayer capacity of adsorbate
V_{liq}	volume of liquid N ₂
V_{ads}	volume of nitrogen adsorbed
P_a	ambient pressure
r_k	Kelvin radius of the pore
γ	surface tension
E_k	kinetic energy
h	Planck's constant
ν	frequency
E_b	binding energy

Greek

ϕ	work function of spectrometer
λ	wavelength of X-ray beam
θ	angle of incidence
β_d	true line width at half maximum intensity
β_{ob}	observed width at half maximum intensity
β_{inst}	instrumental line width by standard

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Disperse X-ray
TGA	Thermogravimetric analysis
POR	Partial Oxidation Reforming

CHAPTER 1

INTRODUCTION

1.1 Background

The demand for the hydrocarbon based compound as primary source of fuel has been on the rise in particular among the developing countries. This has led to unsustainable, uncontrolled exploration and exploitation of the non-renewable fossil fuel in order to support the industrial needs of the nation. Consequently, it causes the dwindling of petroleum reserves and inflicts severe environmental pollution as well as an excessive emission of greenhouse gases (CO_2 and CH_4). In replacement, glycerol (a bio-waste generated from biodiesel production) has been touted as a promising bio-hydrogen precursor via steam reforming route. Alternatively, dry (CO_2)-reforming of glycerol may provide another reforming route.

Hydrogen (H_2) has been considered as energy of future to substitute fossil fuel utilization. The increasing demand for H_2 for industrial and residential markets will provide a quantum leap towards hydrogen economy. H_2 is currently produced from hydrocarbon reforming (i.e. natural gas and petroleum) and electrolysis processes. Unfortunately, CO_2 produced by fossil fuel steam reforming has contributed to greenhouse effect. Therefore, new processes which are more environmentally friendly and economical for hydrogen production are clearly required. Glycerol ($\text{C}_3\text{H}_8\text{O}_3$), which is a byproduct of biodiesel production via alcohol trans-esterification of vegetable oils (triglycerides) has been considered as an excellent candidate for H_2 production. The $\text{C}_3\text{H}_8\text{O}_3$ utilization to produce H_2 or synthesis gas could potentially reduce the production costs of biodiesel.

Synthesis gas is a fuel gas mixture consists of carbon monoxide and hydrogen vital valuable feedstock in the downstream petrochemical industries, production of ammonia, methanol and etc. Furthermore, renewable energy has become a special interest in

nowadays society since the demand for energy resources increases rapidly. Synthesis gas plays a significant role in resolving the above mentioned issues. Synthesis gas can be used as an energy source for power plants generation. Besides, a wide range of synthetic products can be produced from the synthesis gas like clothes, solvents and fuels. Thus, it commands a high demand in the industry. In particular, synthesis gas is an important ingredient for major chemical intermediate in chemical processes for the synthesis of several fuels and chemicals (Wang et al., 2009).

As aforementioned, synthesis gas can be produced from natural gas, petroleum and its derivatives, biomass and coal via many routes. One of them is through the dry reforming of biomass such as glycerol. Significantly, glycerol reforming with CO₂ could be an attractive process although little is known about it. Since the bio-derived glycerol is considered to be renewable and CO₂-neutral, therefore by convention it will not contribute to the greenhouse effect. Secondly, glycerol dry reforming will convert CO₂ into synthesis gas or high value-added inert carbon and remove it from the carbon biosphere cycle (Wang et al., 2009).

Catalysts play a particular important role in this reaction. Normally it is comprised of a promoter, an active metal and also support. Promoter can strongly influence the physicochemical and catalytic property of the catalysts. Moreover, catalyst has a rich history of facilitating energy-efficient selective molecular transformations and contributes to 90% of chemical manufacturing processes and to more than 20% of all industrial products. In a post-petroleum era, catalysis will be central to overcoming the engineering and scientific barriers to economically feasible routes to biofuels and chemicals (Wilson et al, 2012). However, significantly previous studies have indicated that carbon deposition was the major performance-limiting factor for nickel (Ni) catalyst during glycerol steam reforming.

Therefore, in current research magnesium oxide (MgO)-supported Ni catalysts with cerium as promoter were prepared from wet co-impregnation method for the use in dry reforming of glycerol reaction. Thus, different loadings of cerium metal will be

incorporated in the catalyst formulation and tested with different flow rate and temperature in order to determine the optimum glycerol conversion that can be achieved. After that, the catalyst will be characterized with various techniques such as X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET) method and Thermogravimetric Analysis (TGA). The main purpose of performing these techniques is to study the physicochemical properties of catalysts.

1.2 Problem Statements

In spite of the great benefits which can be gained from H_2 gas production via reforming method, there are still many areas of uncertainty and these problems need to be solved before this application can be proceed commercially. There are also several issues or motivations behind the proposition for the current research that need a serious attention from researcher to ensure that this new technology is feasible in industry. Below are some issues that faced by most of the researchers:

- The current commercialized CH_4 steam reforming reactions with Ni based catalyst is not able to achieve conversion over 80% unless in extreme temperature conditions ($> 800\text{ }^{\circ}\text{C}$).
- The thermodynamic, kinetics and characterization of glycerol dry reforming are not known as all prior published works are related to glycerol steam reforming.
- Carbon deposition behavior that leads to catalyst deactivation for most of the carbon containing reactants in particular glycerol is not well studied.
- Commercial process for syngas production by steam reforming leads to CO_2 formation which is not environmental friendly because CO_2 is a greenhouse agent.

1.3 Objectives

The current research aims to synthesize magnesium oxide-supported nickel catalyst promoted with cerium for the application in speeding up H₂ production via glycerol reforming.

1.4 Scopes

In order to achieve the aforementioned objective, the following scopes have been identified:

- I. To prepare Ce-Ni/MgO catalyst with the 3% loadings of Ce via co-impregnation method.
- II. To characterize the catalyst with various techniques such as:
 - X-ray diffraction (XRD) for crystallinity.
 - Scanning Electron Microscopy (SEM) for surface morphology.
 - Brunauer Emmett Teller (BET) method for surface area.
 - Thermogravimetric Analysis (TGA) for measuring of weight changes of solid samples using.
- III. To study the glycerol reforming reaction in a fixed bed reactor at 1 atm and reaction temperatures of 650 to 750°C.

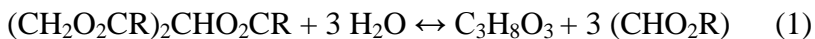
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Glycerol (also known as glycerine) is a by-product of biodiesel production process. Biofuels like ethanol and biodiesel are gaining significance due to the consistent decline in fossil fuels such as oil and natural gas reserves globally. Glycerol will be abundantly available as a by-product in lieu of the commercialization of biodiesel production. This has prompted researchers to find ways for utilization of glycerol to valuable products. Researchers working in the field of hydrogen and syngas production have now started focusing on the use of glycerol for hydrogen and syngas production by various techniques (Kale & Kulkarni, 2010).

Chemically, biodiesel is derived from fats and oils via trans-esterification method. Fats and oils are esters of the tri-alcohol, also commonly called triglycerides. This hydrolysis reaction produces glycerol and fatty acids, which are carboxylic acids derived from fats and oils. In the fatty acids, R represents groups of carbon and hydrogen atoms in which the carbon atoms are attached to each other in an unbranched chain. The reaction of the triglyceride in the reactor is the hydrolysis of the ester groups as shown in equation below:



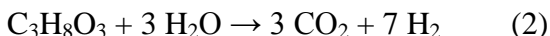
The bio-derived glycerol can be converted to synthesis gas via dry reforming and then used in Fischer-Tropsch synthesis (FTS), which can produce a large variety of hydrocarbons ranging from light gases to heavy wax. Liquid fuels from this biomass material provide renewable routes for fuel production (Wang et al., 2009). Synthesis gas is a major ingredient for many downstream petrochemical processes. Conventional production of syngas is via natural gas steam reforming. However, fossil hydrocarbons

resources are decreasing in the face of growing demand from developing countries; consequently resulting in a spike to energy price.

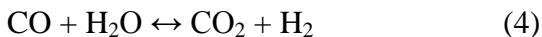
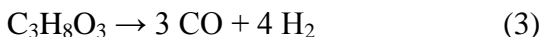
In this ensuing section, previous studies related to the reforming reaction, research catalysts, as well as catalyst deactivation phenomenon are presented.

2.2 Steam Reforming Reaction of Glycerol

Generally, glycerol can be converted into syngas by steam reforming process according to the follow reaction:



This overall reaction can be written as two separate reactions, viz. glycerol decomposition to hydrogen and carbon monoxide (Equation (2)) followed by water-gas shift reaction (Equation (3)):



Cichy & Borowiecki (2008) stated that many catalytic systems used for glycerol steam reforming can be grouped under metals such as Ru, Rh, Ir, Pd, Pt, and Co. In addition, different supports were also used such as CeO₂, Al₂O₃, MgO, TiO₂ and ZrO₂. The most investigated catalysts are those based on Ni. Literature review shows that the addition of promoters to the nickel catalysts has improved their properties such as resistance to coking (K, Mo) and thermal stability (La, Ce). The researches on steam reforming with supported nickel as the catalyst have identified that it not only economical but also perform high steam reforming (Sanchez et al., 2010). Actually, the nickel catalyst has been regularly utilized as catalyzed in petroleum and natural gas processing industry because of its low cost and with the supported nickel used in reforming process; it is believed that the glycerol steam reforming can be commercialized too instead of methane (Trimm et al., 2004). It is economical for country that is abundance with waste glycerol such as Malaysia. However, the main problem faced by steam reforming is its intense

endothermic reaction which requires a lot of energy within the steam reforming reactor and normally this reaction is suitable for large-scale productions only.

2.3 Dry Reforming Reaction of Glycerol

The carbon neutral reforming or dry reforming of glycerol is industrially beneficial compared to steam reforming method in syngas production with greenhouse gas CO₂ could convert into synthesis gas or high value-added inner carbon. Besides, Wang et al., 2009 found that with a temperature of 1000 K and CO₂ to glycerol ratio of 1, the production of synthesis gas reaches a maximum with (H₂:CO = 1) can be produced per mole of glycerol with CO₂ conversion of 33%. The main reaction of dry reforming process is shown on the following equation:



The Equation (6) is the glycerol decomposition to hydrogen or synthesis gas and carbon monoxide and followed by production of methane which is shown by Equation (6). It is believed that the reaction cannot be shifted by changing the molar ratio of reactants when equilibrium constant K_p is much larger than 1, whereas when K_p is approaches 1, the molar ratio of reactant impacts the reaction trend significantly. For a multi-reaction system, the optimized target product mainly depends on the reactions with high K_p . Equilibrium constants of Equation (6) are great enough for complete decomposition of glycerol (Wang et al., 2009). In contrast, many preliminary researches have been done by using simple hydrocarbon fuel such as methane to produce synthesis gas via dry reforming and many papers have been published on methane catalytic dry reforming while glycerol dry reforming is not yet much published (Gao et al., 2011). Hence, a lot of data is still remaining unknown for dry reforming using glycerol. However, there is an

important drawback from the dry reforming method that may lead to a higher rate of carbon deposition and cause catalyst deactivation via coking (Gallego et al., 2008).

2.4 Partial Oxidation Reforming

The syngas production which requires oxygen and hydrocarbon raw materials in the reaction is referred as partial oxidation. This reaction is illustrated in the equation (8). The partial oxidation process is determined to have potential to replace the steam reforming method which is highly endothermic. This process usually requires external cooling as it is highly exothermic while operating at a higher temperature than the steam reforming method (Lucrecio, 2007). The carbon deposition and sulphur poisoning issues in syngas production process can be overcome by using high temperature in partial oxidation method. Moreover, the partial oxidation process for syngas production does not require water supply system like in steam reforming method and hence, reducing the production cost.

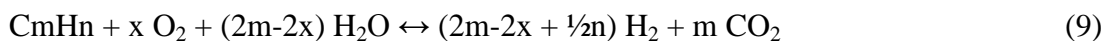


As the partial oxidation method for syngas production is characterized as an exothermic reaction, its reactor can be started faster than the steam reforming reactor. Therefore, the partial oxidation reactor does not require heat transfer optimization which can be designed to be lighter and in a more compacted size. In other words, the partial oxidation method is suitable to be used in a smaller system. Besides that as the partial oxidation reaction is exothermic, adiabatic reactor can be used for methane partial oxidation process. It has been determined that the stoichiometric of the partial oxidation reaction according to the equation (4) has a product molar ratio of H_2/CO equals two. This product molar ratio is suitable for Fisher-Tropsch and methanol synthesis. Moreover, the high operating temperature of partial oxidation process is favourable to be used for the solid oxide fuel cells as it will hinder the CO poisoning of the fuel cells. Apart from that, partial oxidation process is also a catalytic synthesis process and supported nickel is the catalyst that has been widely used for the

process, same as steam reforming method because of its high catalytic activity and low cost. Anyway, it has been reported that the amount of hydrogen gas that is generated by partial oxidation reaction is lower than the steam reforming reaction. Besides, the overall energy consumption and production cost of the partial oxidation reaction will be higher than steam reforming method. Hence, the partial oxidation method is still not the best method for syngas production in industry.

2.5 Auto-thermal Reforming

It has been reported that steam reforming method produces higher efficient and yield of synthesis gas but is unsuitable for portable unit application because of its high endothermic reaction. On the other hand, partial oxidation has lower yield of hydrogen gas and its operating system is too high to be commercialized. Anyway, it is suitable as if the system is small. Meanwhile, auto-thermal reforming is the method that uses the combination of partial oxidation method and steam reforming method which is shown in equation (9) (Nilsson et al., 2009). Hence, the auto-thermal reforming process possesses higher synthesis gas production efficiency and simple system design which require lower investment than other processes. The main mechanism of the auto-thermal reforming method is also showed by equation (9) below.



The 'x' is the variable that represents the oxygen-to-fuel ratio which is used as the auto-thermal reforming's heat transfer controller. For instance, the overall reaction will be partial oxidation dominant and become more exothermic when the value of x is higher. Meanwhile, the overall reaction will be steam reforming dominant and become more endothermic when the value of x is lower. In other words, the x value is used to adjust the overall reaction either towards exothermic or endothermic, depends to requirement. Anyway it has been reported that the overall reaction will be controlled to be a bit more towards exothermic to enable self-sustenance of the reactor (Kang & Bae, 2006). Therefore unlike steam reforming, auto-thermal reforming does not

require heat from outer source and its operating temperature is normally lower than the partial oxidation method for synthesis gas production. Then, another ratio which can be controlled is the steam-to-fuel ratio for different product composition. In order to produce higher hydrogen yield, the steam-to-fuel should be higher. The addition of steam in the reaction helps in its water-gas-shift mechanism and leads to higher hydrogen production while additional of oxygen can lower the coke formation possibility and make the reaction faster. It is determined that although auto-thermal reforming method is the combination of partial oxidation method and steam reforming method, the reactions take place in sequence, where partial oxidation reaction occurs following by the steam reforming reaction and, so the auto-thermal reforming reaction can be initiated in a fast rate (Lim et al., 2009). In other words, the auto-thermal reforming method contains the advantages from both steam reforming and partial oxidation method (Escritori et al., 2009). However it is reported that, the concentration of hydrogen within the production from the auto-thermal reforming method is just in between partial oxidation and steam reforming method, meaning that it still lower than the gas generation from steam reforming.

2.6 Thermodynamics Analysis of Reactions in Glycerol Dry Reforming

Table 2.1 below show the main reactions which may occur in CO₂ reforming of glycerol.

Table 2.1: Reactions in CO₂ reforming of glycerol (Wang et al., 2009)

Possible reactions	ΔH_{298K} (kJ/mol)	No. of Equation
$C_3H_8O_3 \leftrightarrow 4H_2 + 3CO$	251.18	(11)
$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-206.11	(12)
$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-164.94	(13)
$CO_2 + CH_4 \leftrightarrow 2H_2 + 2CO$	247.28	(14)
$CO + H_2O \leftrightarrow H_2 + CO_2$	-41.17	(15)
$C + H_2O \leftrightarrow H_2 + CO$	131.26	(16)



Figure 2.1 shows the equilibrium constant of reactions involving in glycerol – CO₂ reaction at different temperatures and atmospheric pressure.

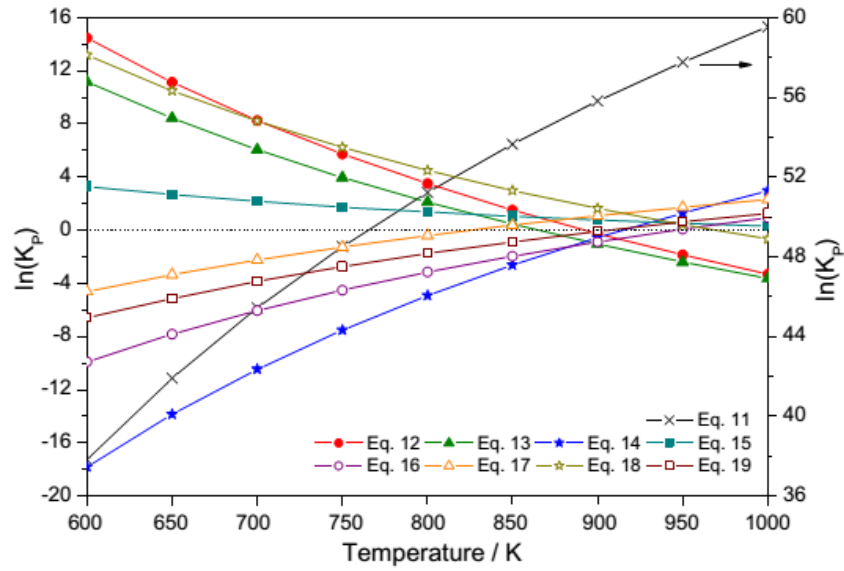


Figure 2.1: Equilibrium Constant of Reactions Involving In Glycerol – CO₂ Reaction at Different Temperatures and Atmospheric Pressure

2.6.1 Carbon Dioxide Conversion

As aforementioned, one of important advantages from glycerol dry reforming is that CO₂ can be converted into synthesis gas or sequestered and removed from the carbon biosphere cycle. Therefore, the conversion of CO₂ needs to be considered and discussed. Figure 2.2 shows moles of CO₂ versus temperature at different CGRs. Moles of CO₂ at equilibrium reach a maximum between 750 K and 825 K regardless of CGRs. This can be

ascribed to the reformation of CO_2 with CH_4 . High temperature favours the conversion of CO_2 . For CGRs 1–5, the conversion of CO_2 reaches 30–39% over 950 K. While for other CGRs considered in this work, the moles of CO_2 at equilibrium are more than initial input quantities (Wang et al., 2009).

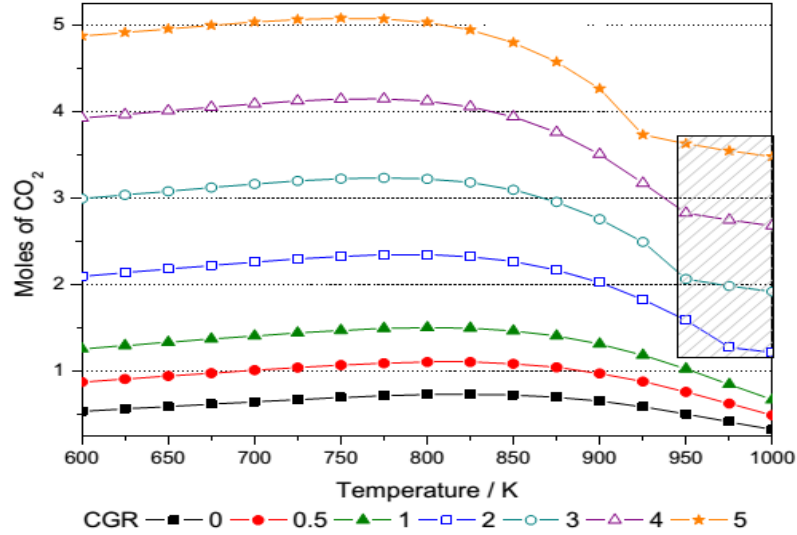


Figure 2.2: Moles of Carbon Dioxide as a Function of CGR and Temperature at Atmospheric Pressure, $n^0(\text{C}_3\text{H}_8\text{O}_3) = 1 \text{ Mol}$.

2.6.2 Hydrogen and Synthesis Gas Production

Figure 2.3 depicts the production of hydrogen and synthesis gas at different temperatures and pressures. Briefly, the amount of hydrogen and synthesis gas produced decreases with the increase in pressure. Therefore, Wang and his partners selected atmospheric pressure as the best one with respect to hydrogen and synthesis gas production all through following discussions. As can be seen from Figure 2.4, moles of hydrogen increase with increasing temperature all the way when CGR is < 1 , whereas with CGR higher than 1, the number of moles of hydrogen increases with increasing temperature, goes through a maximum around 925–975 K, and then decreases at higher temperatures. Moles of

hydrogen decrease together with CO₂ over temperatures at which hydrogen production maximizes, while moles of water and CO increase. This probably can be explained by reaction (15). The effect of CGR on hydrogen production is not significant when it is < 2, but high CGRs reduce the capacity of hydrogen production when temperature is higher than 925 K. More than 3 moles of hydrogen can be generated at CGRs between 0 and 1 over 975 K. The amount of hydrogen produced in glycerol dry reforming is less than those reported previously (Wang XD et al., 2008; Adhikari et al., 2007). The K_p s associated with reactions involving H₂ are plotted in Figure 2.1. It can be seen that reaction (11) proceeds more easily with the entire considered temperature range. The reversion of reaction (14) is feasible below 800 K and then limited by equilibrium. Reactions (12), (13), (16), and (19) are affected by equilibrium limitations when temperature is higher than 700 K. Reactions (15) and (17) are limited within the whole investigated temperature range.

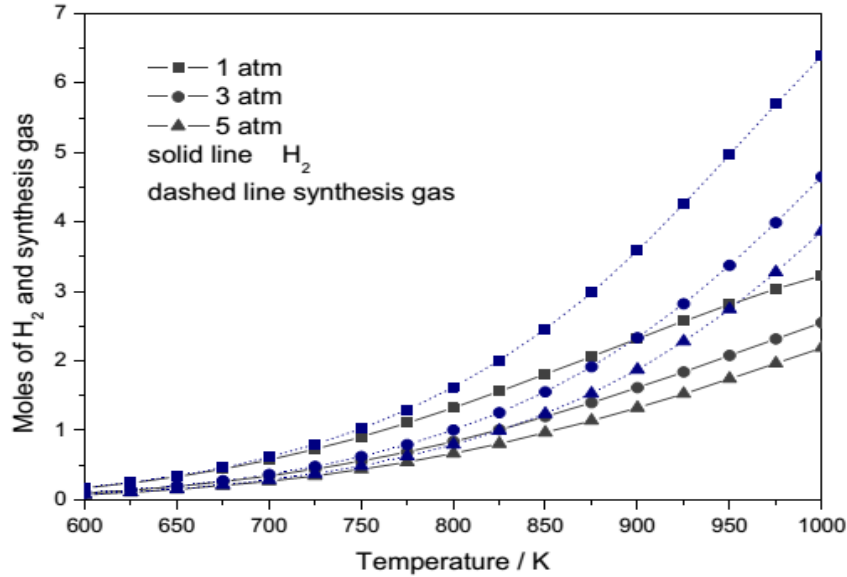


Figure 2.3: Moles of Hydrogen and Synthesis Gas Produced at Selected Pressures and
CGR = 1, $n^0(\text{C}_3\text{H}_8\text{O}_3) = 1 \text{ Mol}$

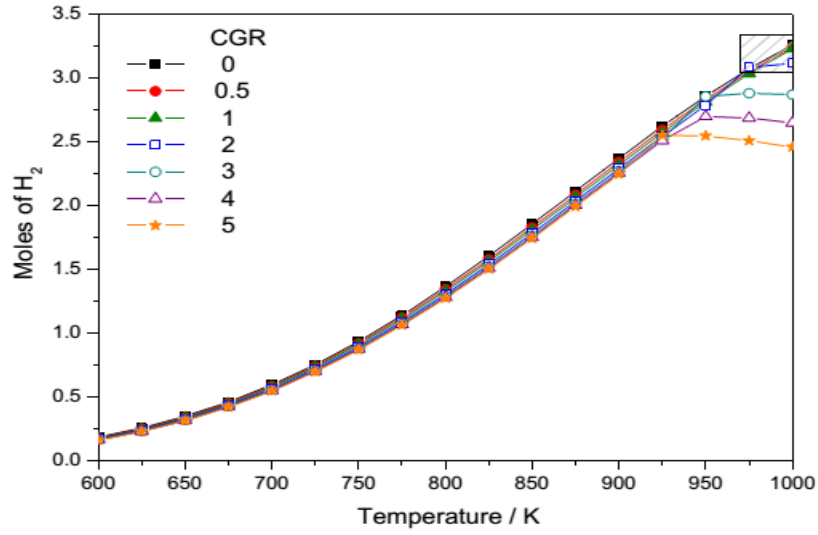


Figure 2.4: Moles of Hydrogen as a Function of CGR and Temperature at atmospheric Pressure, $n^0(\text{C}_3\text{H}_8\text{O}_3) = 1 \text{ Mol}$

Figure 2.5 shows moles of CO as a function of CGR and temperature at atmospheric pressure.

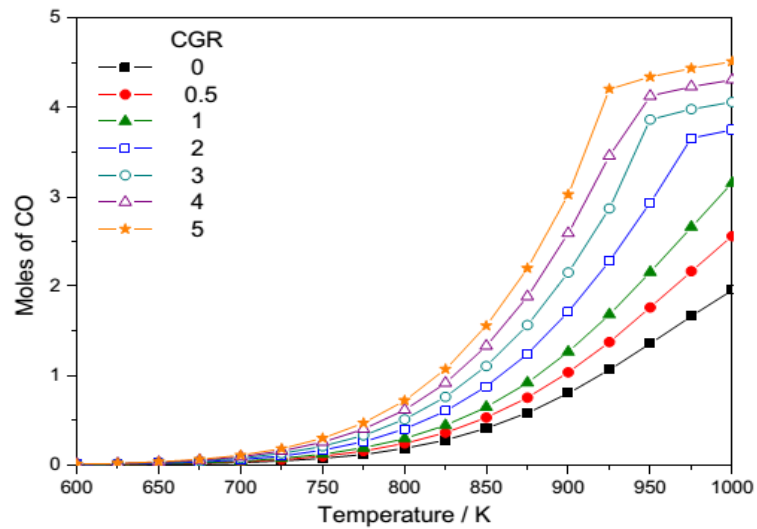


Figure 2.5: Moles of Carbon Monoxide as a Function of CGR and Temperature At Atmospheric Pressure, $n^0(\text{C}_3\text{H}_8\text{O}_3) = 1 \text{ Mol}$.